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Supplementary and Additional Material

Hydrophobic molecules slow down the hydrogen-bond dynamics of liquid water

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1. Description of global-fit procedure for the results of slope analysis

It is generally accepted that the frequency dynamics of the OH stretching mode of the HDO molecule in the D₂O bath can be approximated by two exponential decays with ~ 0.15 ps and ~ 1 ps times [1] [2]. The former component is usually associated with the combined action of water librations and intramolecular O-O stretch vibrations while the latter represents the translational motion of waters and/or rearrangements of the hydrogen-bond network. From the experimental data of the slope transients (Fig.SM1, left panel) we can conclude that the initial (librational) part does not show any substantial changes with solute concentration. In contrast, the second, slower contribution does change strongly upon addition of the amphiphilic solutes. To describe the slope data quantitatively with a minimal number of free parameters, we use the following *ad hoc* functional dependence of the slope values:

$$S(T) = A_1 \cdot \exp\left(-\frac{T}{\tau_1}\right) + A_2 \cdot \exp\left(-\frac{T}{\tau_2}\right) + A_0,$$

where A_1/τ_1 stand for the amplitude/time constant of the fast dynamics, A_2/τ_2 characterize the amplitude/time of the slower dynamics of the water, and A_0 stands for the amplitude of water molecules that are strongly slowed down in their spectral dynamics. It should be noted that the time span of the 2D experiments does not allow for a reliable determination of the time scale of spectral diffusion of the slowed down molecules, which is therefore represented by an offset A_0 .

We performed a global fit analysis to the slope value time dependences for *all* three solutes at *all* concentrations. We obtain high-quality fits for all three solutes at all measured concentrations with this limited set of parameters. We found that the introduction of a larger number of fitting parameters (like, for instance, concentration dependent time τ_1) would make the global fitting unstable. In the fit we keep the parameters A_1, τ_1 and τ_2 global (i.e. identical for all 12 transients). The fits for TMU, TBA and TMAO are shown in Fig. SM1 and the resulting fit parameters are listed in Table SM1. The obtained time constants $\tau_1 = 0.15$ ps and $\tau_2 = 0.78$ ps are very much in line with the published literature data for HDO:D₂O [1-3]. As expected, with increasing solute concentration, the amplitude A_2 diminishes while the offset values A_0 increases (Fig. SM1, right panel).

2. References

- 1) Yeremenko, S., Pshenichnikov, M.S., & Wiersma, D.A., Hydrogen-bond dynamics in water explored by heterodyne-detected photon echo. *Chem. Phys. Lett.* 369, 107–113 (2003).
- 2) Tokmakoff, A., Shining light on the rapidly evolving structure of water. *Science* 317 (5834), 54-55 (2007).
- 3) Asbury, J.B. *et al.*, Dynamics of water probed with vibrational echo correlation spectroscopy. *Journal of Chemical Physics* 121 (24), 12431-12446 (2004).

Table SM1. Parameters of global fit of slope decays. The resulting values of the global (i.e. identical for all concentrations/solutes) parameters are $A_1 = 0.26$, $\tau_1 = 0.15 \text{ ps}$; $\tau_2 = 0.78 \text{ ps}$.

Values of A_2 :

w	0	0.05	0.1	0.2	0.5	1
TMU	0.34	0.29	0.17	0.1	0.08	0.05
TMAO		0.21	0.2	0.04	--	--
TBA		0.21	0.19	0.13	--	--

Values of A_0 :

w	0	0.05	0.1	0.2	0.5	1
TMU	0 (fixed)	0.16	0.27	0.34	0.39	0.4
TMAO		0.1	0.23	0.48	--	--
TBA		0.13	0.24	0.32	--	--

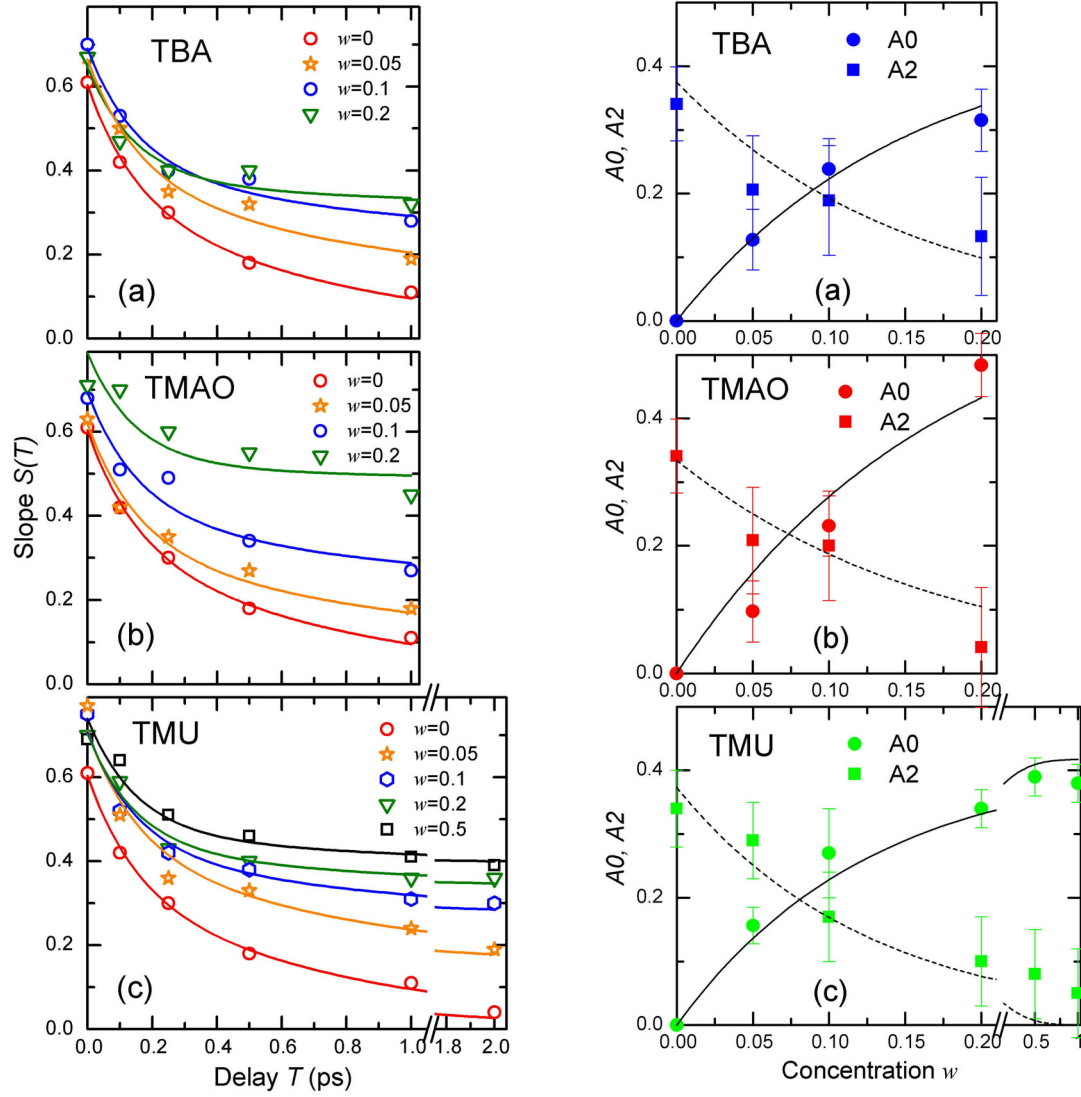


Figure SM1. (left column): Results of the global fit procedure on the slope transients for TBA (a), TMAO (b), and TMU (c). The symbols show the results of the slope analysis of the experimental 2D spectra at different concentrations w , while the solid curves are the fit results. The fit parameters are given in Table SM1. For a detailed description of the fit procedure, see the text.

(right column): Graphical representation of the global fit parameters A_0 (circles) and A_2 (squares) from Table SM1 as a function of concentration w for TBA (a), TMAO (b), and TMU (c). The curves present fit results with functions $A_0 = A' \cdot [1 - \exp(-w/w_0)]$ (solid) and $A_2 = A'' \cdot \exp(-w/w_0)$ (dashed).